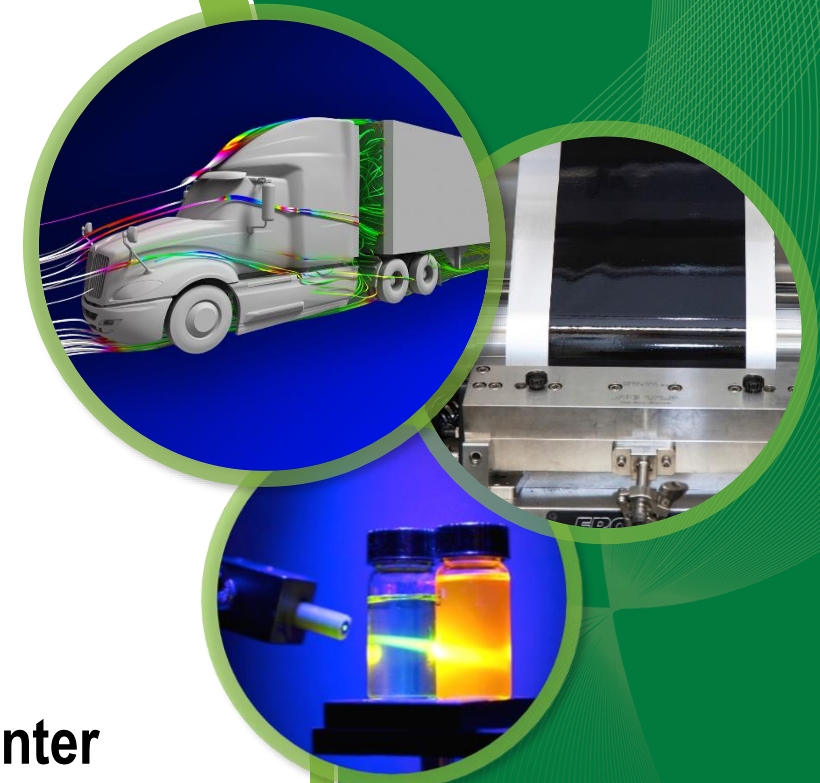
Thick Low-Cost, High-Power Lithium-Ion Electrodes via Aqueous Processing



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Oak Ridge National Laboratory

National Transportation Research Center

2018 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 19, 2018 **Project ID: BAT164**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Task Start: 10/1/14
- Task End: 9/30/19
- Percent Complete: 70%

Barriers

- Barriers Addressed
  - **By 2022, further reduce EV battery-pack cost to $80-100/kWh.**
  - **Advanced Li-ion xEV battery systems with low-cost electrode architectures.**
  - **Achieve deep discharge cycling target of 1000 cycles for EVs by 2022.**

Budget

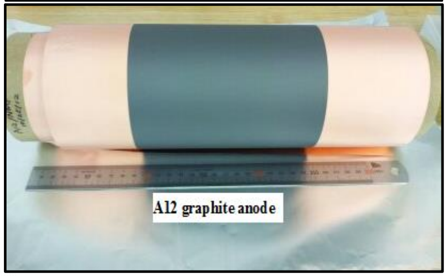
- Total task funding
  - $3600k
- $700k in FY16
- $700k in FY17

Partners

- Interactions/Collaborations
  - National Laboratories: ANL, SNL, INL
  - Universities: KIT, SUNY-Binghamton
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Material/Process Suppliers: PPG Industries, TODA America, Superior Graphite, ConocoPhillips, IMEYS, JSR Micro, Solvay Specialty Polymers, Ashland, PneumatiCoat
  - Equipment Manufacturer: Frontier Industrial Technology, B&W MEGTEC, DataPhysics
- Project Lead: ORNL

Relevance & Objectives

- Main Objective: To improve cell energy and power density and reduce battery pack cost by manufacturing thick electrodes with tailored electrode architecture via aqueous processing and utilizing high energy high voltage cathode materials.
- Objectives in this period
  - Fabricate thick and crack-free composite cathode via aqueous processing
  - Create laser structured electrodes
  - Evaluate compatibility of high Ni-NMC with aqueous processing
  - Investigate potential application of aqueous processing for high Ni-NMC
  - Characterize surface energy of electrodes
  - Demonstrate energy density ≥225 Wh/kg (cell level)



Project Milestones

Status	SMART Milestones	Description
9/30/17	Go/No-Go Decision (Go)	Gen 1 Cathode Performance Criteria: complete 1.5-Ah pouch cell rate performance, low-rate cycling (50 0.2C/-0.2C cycles), and high-rate cycling (150 1C/-2C cycles) for cells with ***combined Gen 1 anode and cathode design of graded electrode architecture*** → improve gravimetric energy density of baseline cell design to ≥200 Wh/kg (cell level) and demonstrate no more than 20% capacity fade through 200 additional 0.33C/-0.33C cycles in 1.5-Ah full pouch cells.
3/31/18 To be completed by June	Annual Milestone (stretch)	Optimize NMC 622 aqueous dispersion formulation(s) for binder and dispersant molecular weight and concentration (with independent carbon nanotube and active material formulations), and quantify dispersion constituent zeta potentials; obtain rate capability data and quantify capacity fade through at least 500 USABC 0.33C/-0.33C cycles while demonstrating an initial cell energy density rating of 225-250 Wh/kg (with upper cutoff voltage of 4.4 V).
3/31/18	Quarterly Progress Measure (Regular)	Demonstrate second round of 2-D and 3-D laser structured electrode samples from KIT in Germany, and quantify rate capability and capacity retention vs. ABR anode and cathode baseline materials.
9/30/18	Go/No-Go Decision	Complete 1.5-Ah pouch cell rate performance, low-rate cycling (50 0.2C/-0.2C cycles), and high-rate cycling (300 1C/-2C cycles) for cells with combined Gen 3 graphite anode and NMC 622 cathode structured designs. Improve gravimetric energy density of baseline cell design to 225-250 Wh/kg (cell level) and demonstrate no more than 20% capacity fade through 200 additional 0.33C/-0.33C cycles.

Project Approach

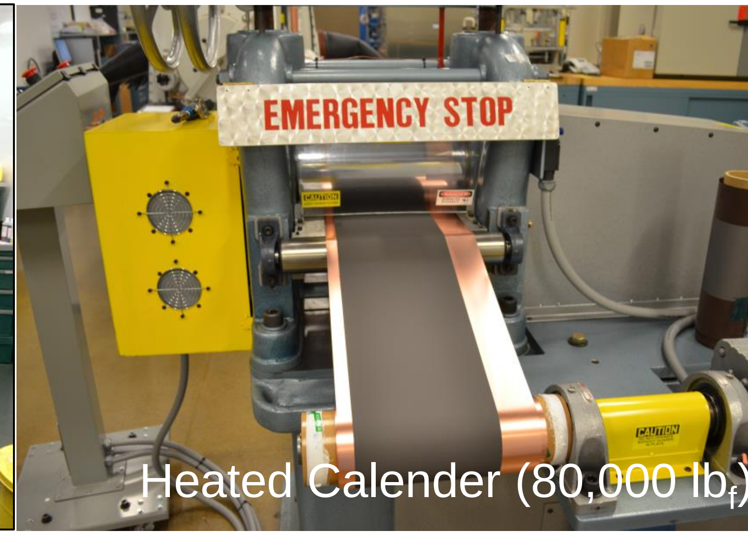
- Problems:
  - Electrode cracking in thick electrodes
  - Mass transport limitations thick electrodes

- Technical approach and strategy:
  - Fabricate crack-free electrodes with high areal loading (4-8 mAh/cm^2) via aqueous processing
  - Create laser structured electrodes to overcome mass transport limitation
  - Simulate energy and power density in laser structured electrodes
  - Evaluate stability of high energy and high voltage cathodes (NMC622 and NMC811) during aqueous processing
  - Incorporate aqueous processing to fabricate NMC811 cathodes
  - Characterize surface energy of composite electrodes and dependence on calendaring to provide insights into electrolyte wetting
  - Characterize electrode microstructure
  - Evaluate rate performance and long term cyclability in pouch cells

Project Approach – Pilot-Scale Electrode Processing and Pouch Cell Evaluation: DOE Battery Manufacturing R&D Facility (BMF) at ORNL

Planetary Mixer (≤2 L)

Dual Slot-Die Coating Line



Heated Calender (80,000 lb_f)

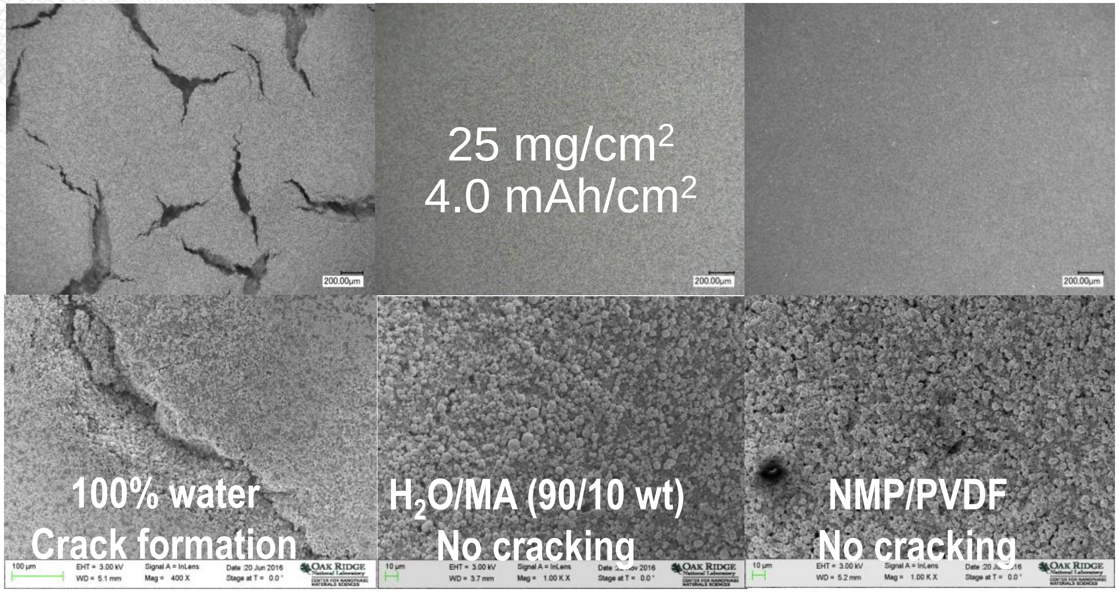
<u>Dry room for pouch cell assembly</u>

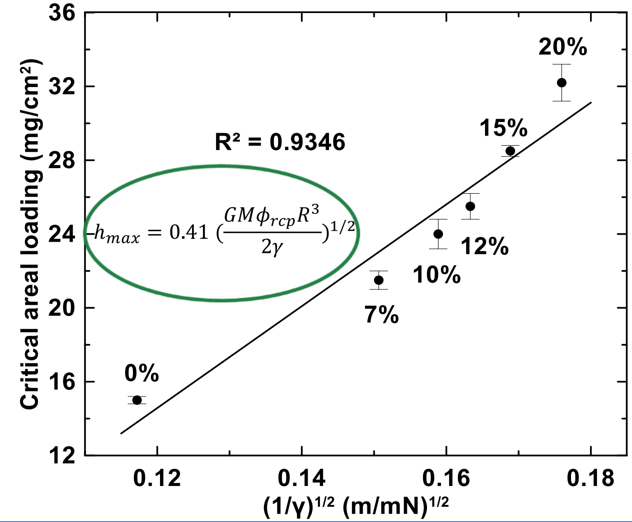
- Largest open-access battery R&D facility in US.
- All assembly steps from pouch forming to electrolyte filling and wetting.
- 1400 ft^2 (two 700 ft^2 compartments).
- Humidity <0.5% (-53°C dew point maintained).
- Pouch cell capacity: 50 mAh – 7 Ah.
- Single- and double-sided coating capability.
- Current weekly production rate from powder to pouch cells is 50-100 cells.

Technical Accomplishments – Executive Summary

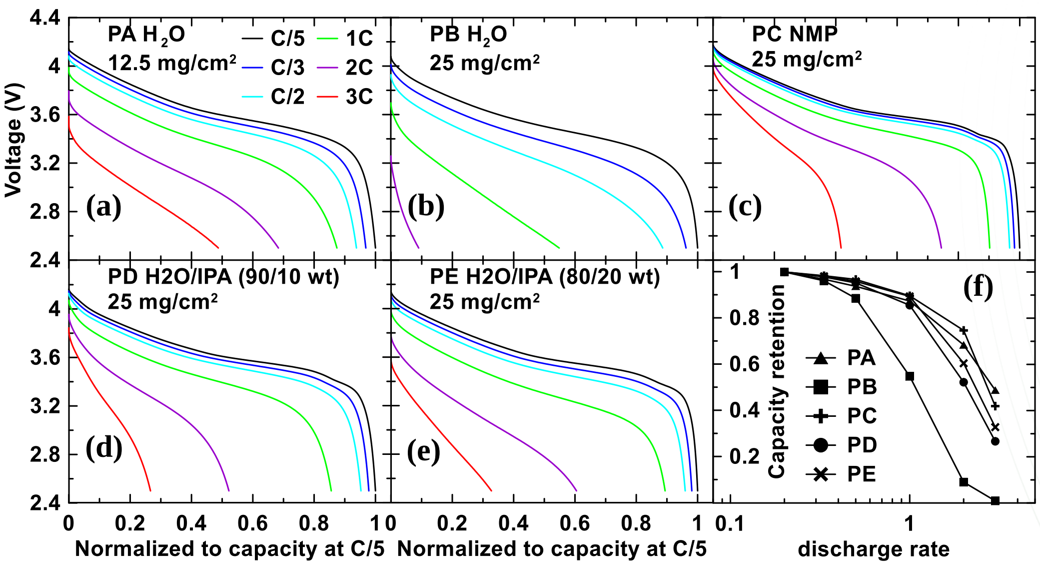
- Demonstrated >80% capacity retention over 700 cycles in NMC532 cathodes processed (4 mAh/cm^2) via co-solvent (H_2O/IPA 9/1).
- Diagnosed capacity fade in NMC532 cathodes processed via H_2O/Methyl Acetate (MA), possibly due to hydrolysis of MA.
- Created laser structured NMC532 cathodes with 2 pitch width in collaboration with KIT, Germany.
- Demonstrated 225 Wh/kg in 14-Ah pouch cells with laser structured and all aqueous processed electrodes.
- Evaluated compatibility of Ni-rich NMC (NMC622 and NMC811) with aqueous processing.
- Demonstrated excellent rate performance and cyclability in aqueous processed NMC811.
- Lower rate performance observed in aqueous-processed cells is mostly due to formulation rather than structural changes
- First ever characterization of the surface energies of NMC532 cathodes and graphite anodes and quantification of reduction in surface energy due to calendering.

Technical Accomplishments—Demonstrated Manufacturing of Crack-Free NMC532 Cathode (4 mAh/cm^2) via Co-Solvent Method (FY17)





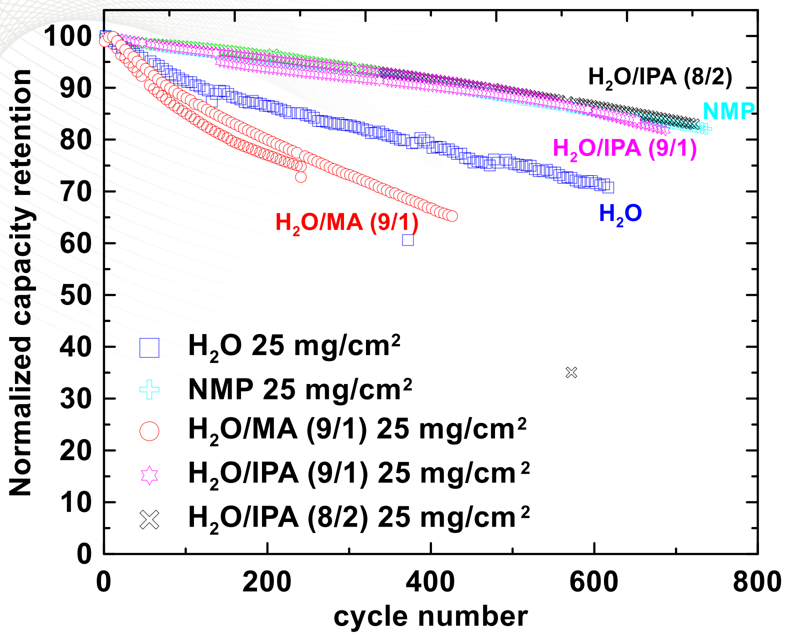
Crack free NMC532 cathodes can be fabricated with H_2O/IPA (8/2 wt) up to 32 mg/cm^2 (5 mAh/cm^2).

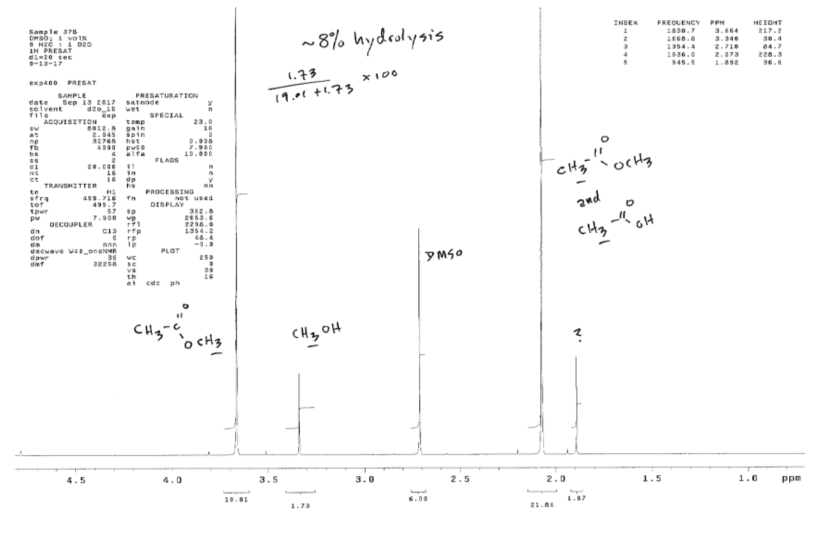


- Demonstrate fabrication of crack free thick NMC532 with co-solvent
- Demonstrated comparable rate performance in co-solvent processed NMC532 cathodes
- Predicted crack-free NMC532 cathodes up to 5 mAh/cm$_2$ with H_2O/IPA (8/2 wt) .

Du et al., *JPS*, 354(2017), 200-206

Technical Accomplishments—Demonstrated >80% Capacity Retention over 700 Cycles (FY18)





- Identical cyclability from electrodes via NMP and H_2O/IPA (9/1; 8/2) with >80% capacity retention over 700 cycles
- However, the cycle life of H_2O/MA (9/1 wt) formulation needs to be improved.

Possible degradation reason:

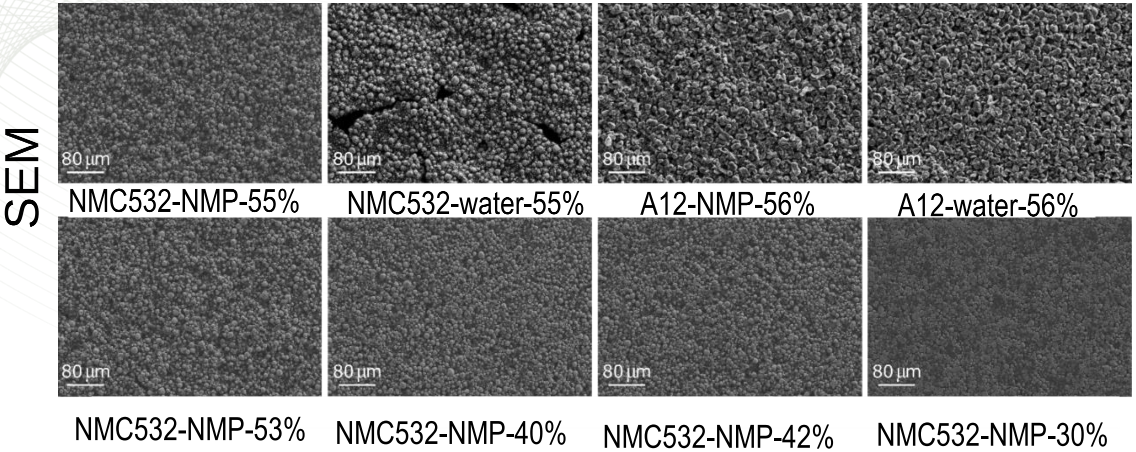
MeOAc+H_2O→MeOH+ AcOH (acid group)

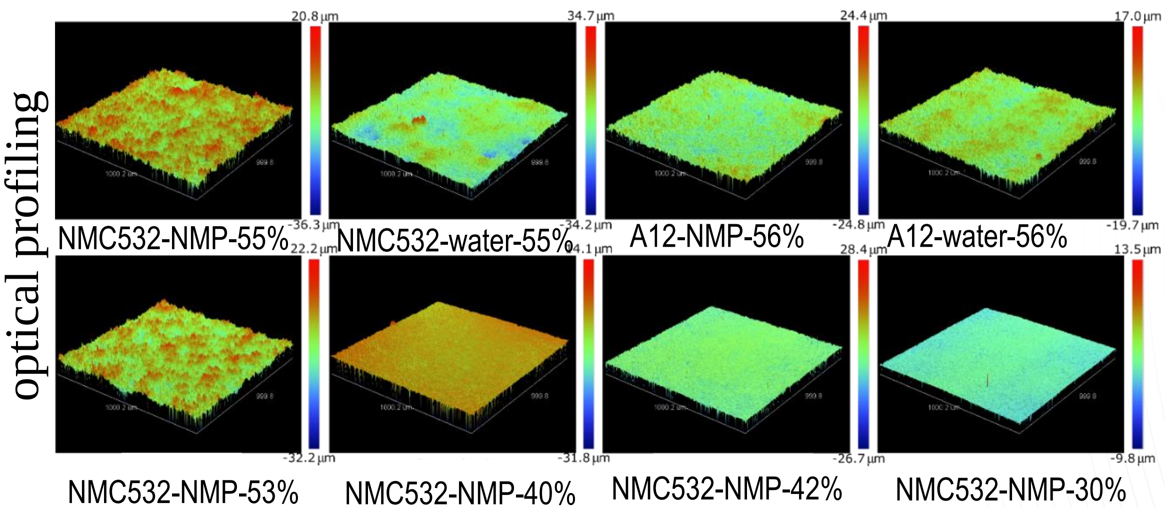
- pH reduces from 12.4 to 9.0 after 4 h mixing of NMC532 with H_2O/MeOAc (90/10 wt%)
- NMR identifies—CH_3COOCH_3;CH_3OH; CH_3COO^-

  Calculated 8% hydrolysis

Du et al., *JPS*, In Press

Technical Accomplishments—Characterization of Surface Solid Ratio and Surface Roughness of NMC532 and A12 Graphite Electrodes (FY18)





Electrode	Solid Surface Fraction (f)	Surface Roughness (r)
NMC532-NMP-55%	0.18	2.47
NMC532-Water-55%	0.35	1.73
A12-NMP-56%	0.18	1.86
A12-Water-56%	0.11	1.80
NMC532-NMP-53%	0.17	2.49
NMC532-NMP-40%	0.41	1.80
NMC532-NMP-42%	0.36	1.90
NMC532-NMP-30%	0.63	1.20
NMC532-Water-46%	0.39	1.71
A12-NMP-44%	0.35	1.72
A12-Water-28%	0.47	1.47

Percentages correspond to porosity

- Surface roughness characterized by OP (optical profilometer), AFM, SP (maximum peak height)
- Surface roughness highly dependent on measurement techniques; OP was selected for high consistency
- Surface solid fraction dramatically different from bulk solid fraction, e.g. relative density

Technical Accomplishments— First Characterization of Surface Energy of NMC532 and A12 Graphite Electrodes to Provide Insights on Electrolyte Wetting (FY18)

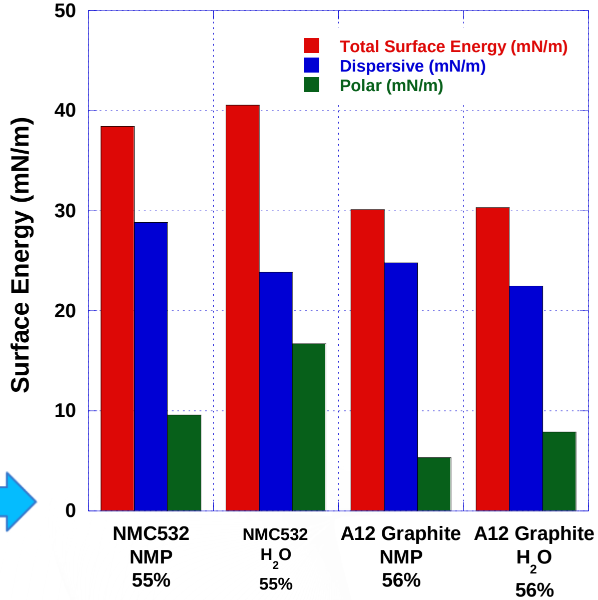
Owens-Wendt-Rabel-Kaelble (OWRK)

$$\sqrt{\gamma_{sv}{}^{D}} + \sqrt{\gamma_{sv}{}^{P}} \sqrt{\frac{\gamma_{lv}^{P}}{\gamma_{lv}^{D}}} = \frac{\gamma_{lv}(1+\cos\theta)}{2\sqrt{\gamma_{lv}^{D}}}$$

$$\cos\theta^{*} = r\cos\theta$$

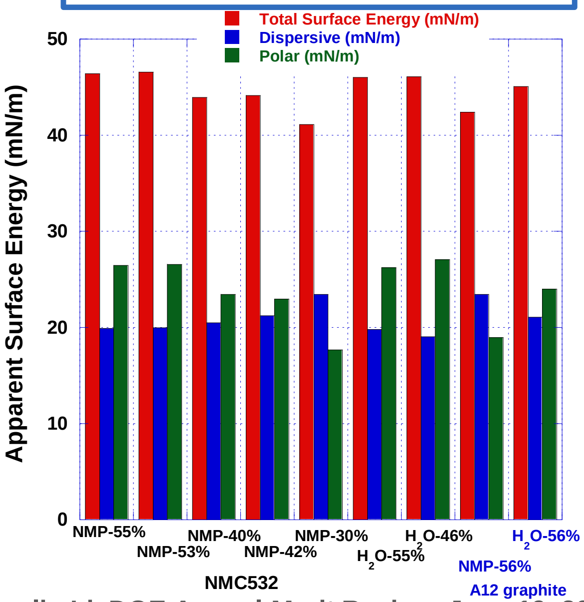
$$\cos\theta^{*} = f\cos\theta + f_2\cos\theta_2$$

θ and θ_2 are the Young's contact angles of pure materials *1* and 2, respectively. ɵ-contact angle; ɵ*-apparent contact angle; *f* and f_2 are the area fractions of material *1* and *2.*



Surface Energy

Apparent Surface Energy



- Static Advancing contact angel is used in calculating surface energy
- Significant improved hydrophilicity in aqueous processed electrodes—74.1% and 48.2% increase for NMC532 and A12 graphite, respectively

- Lower apparent surface energy and polar component with denser electrodes
- Electrolyte wetting measurement ongoing

Li et al., *Under Review*

BINGHAMTON UNIVERSITY STATE UNIVERSITY OF NEW YORK

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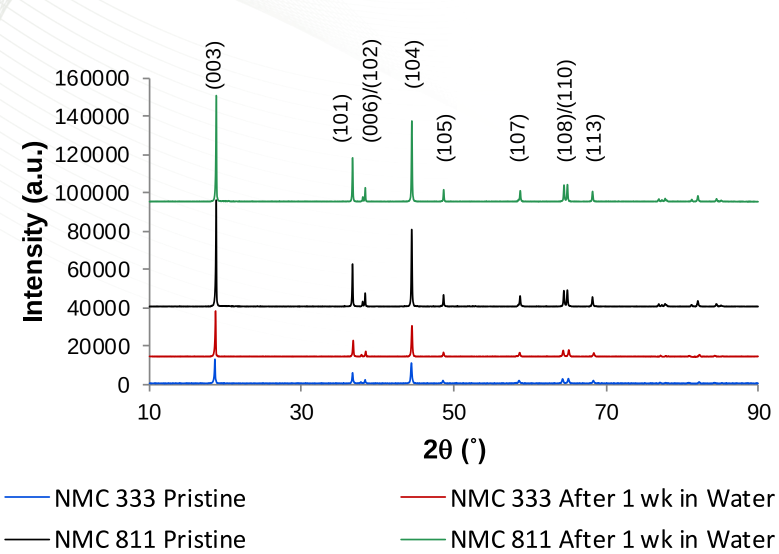
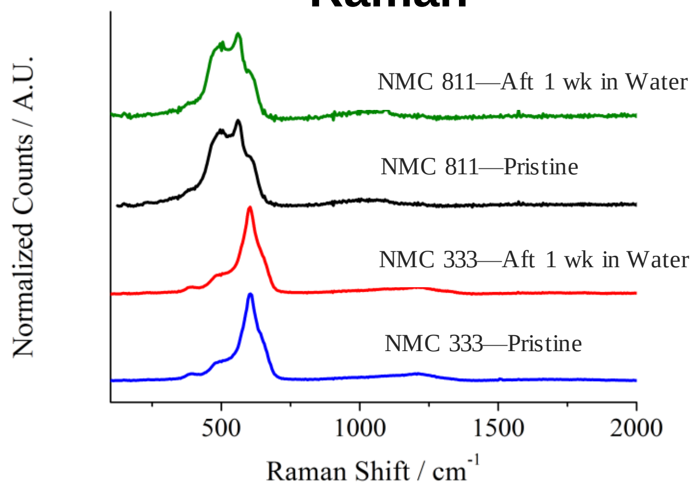
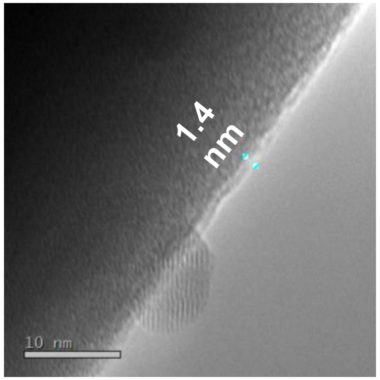
Technical Accomplishments—Evaluation of Compatibility of NMC811 with Aqueous Processing (FY18)



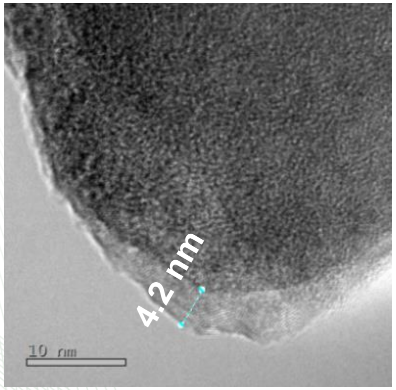


TEM

Pristine



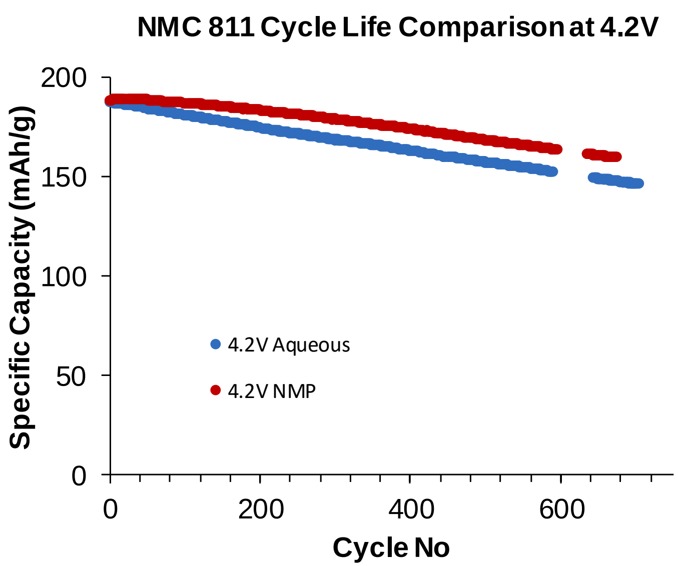
After 1 wk Water High Solids %



- XRD shows no bulk structural changes after water exposure
- Averaged Raman spectra (≥ 100 spots) show no difference before and after water exposure
- There seems a thin layer on some NMC811 particles, which may be getting thicker and more amorphous with increasing water exposure, but results are inconclusive

Technical Accomplishments— Excellent Cyclability from Aqueous Processed NMC811 cathodes (FY18)

- NMC 811 Cathode Recipes:
  - **Aqueous:** 90 wt% NMC 811 / 5 wt% Carbon Black / 1 wt% CMC Binder / 4 wt% Acrylic Emulsion
  - **NMP**: 90 wt% NMC 811 / 5 wt% Carbon Black / 5 wt% PVDF Binder
- Single-layer pouch cells with **aqueous**- and **NMP**-processed NMC 811 cathodes and Superior SLC 1520T graphite anodes
  - NMC 811 Loading: 11.6 mg/cm^2 (aqueous) and 11.3 mg/cm^2 (NMP)
- Water-exposed NMP: NMC811 powder was saturated in water for 4 h, dried, and then fabricated into electrodes with NMP-based processing



- Incorporating aqueous processing with high energy and high voltage cathode for high energy density
- Aqueous-processed cells show excellent cyclability
  - Slightly higher capacity fade than NMP-processed cells after ~650 cycles
  - Faster capacity fade could be due to electrode formulation and/or slurry preparation

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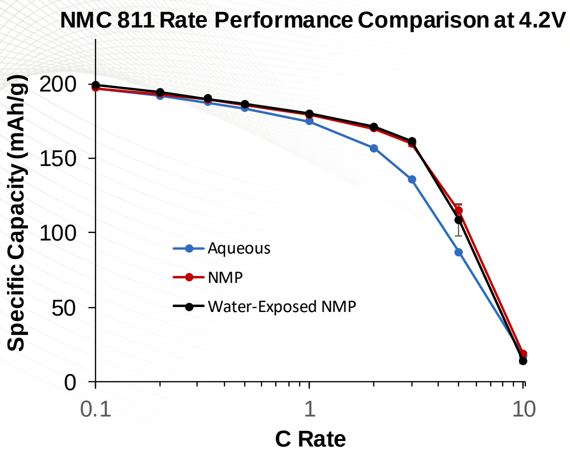
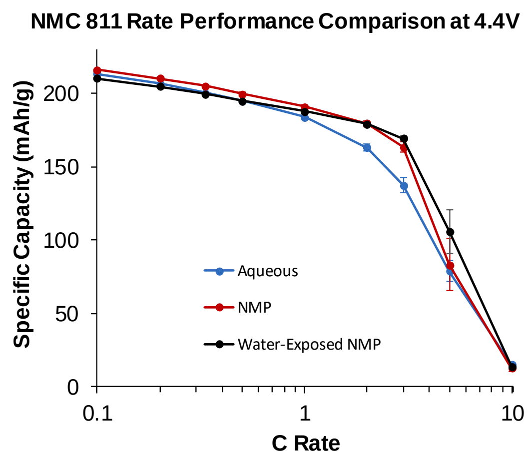
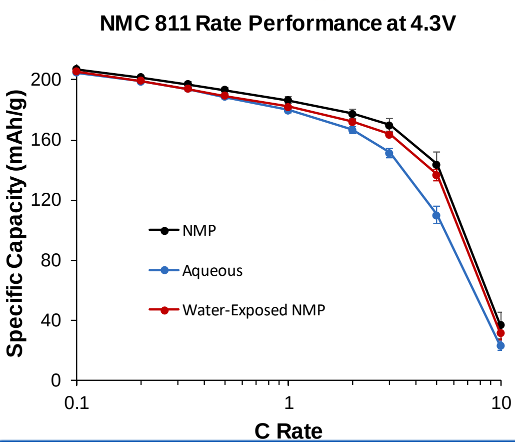
Technical Accomplishments— Excellent Rate Performance from Aqueous Processed NMC811 Cathodes (FY18)

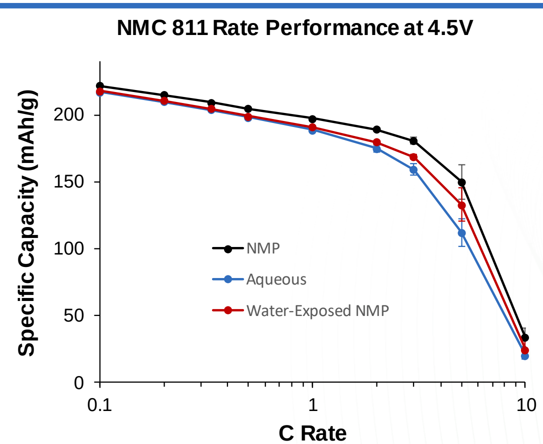




All cells were made in triplicate

Full pouch cells





Full coin cells

- Aqueous-processed cells show identical rate performance with NMP-processed ones up to 1C and are slightly lower at higher C-rates
- Water-exposed NMP-processed cells show almost identical rate performance to NMP-processed cells at various upper cutoff voltages
- Suggests that the lower rate performance observed in aqueous-processed cells is mostly due to formulation rather than structural changes

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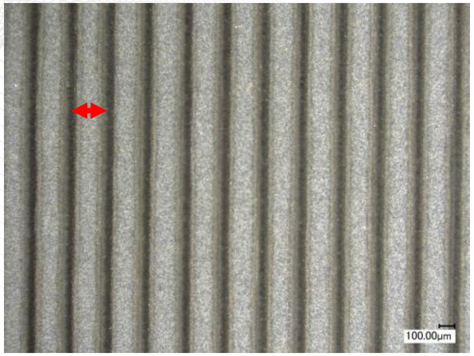
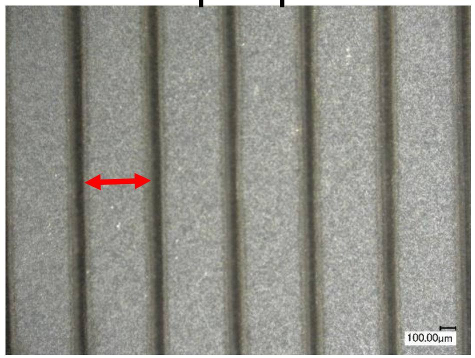
Technical Accomplishments—Demonstrated Laser Structured Electrodes with Improved Rate Performance (FY18)

250µm pitch



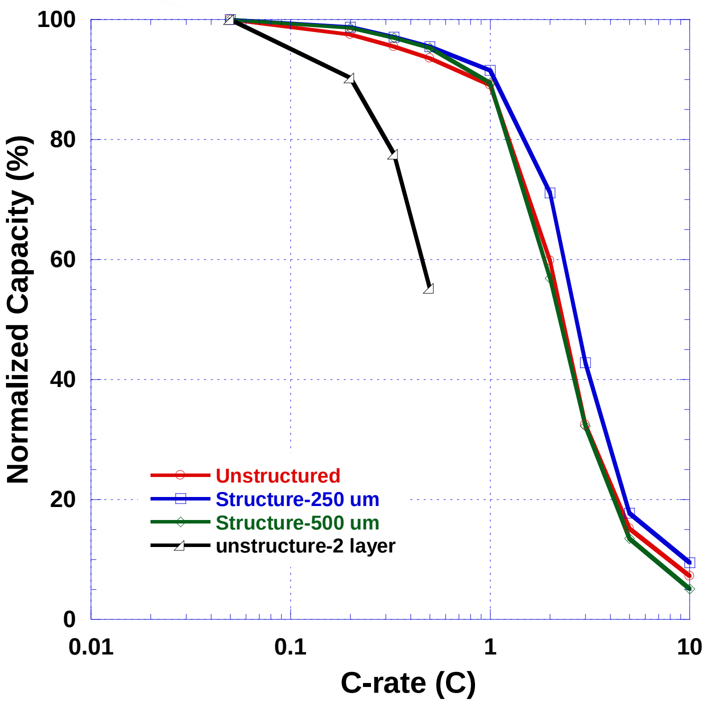
500µm pitch



2-layer structure

NMC532: 13.0 mg/cm^2; 40%
2nd layer

NMC532: 12.0 mg/cm^2; 27%
1st layer



- NMC/carbon black/Binder=90/5/5 wt
- 2-layer NMC532: 25 mg/cm^2; others 29.7 mg/cm^2
- Demonstrated **225** Wh/kg at 14 Ah pouch cell format (110 mm X 148 mm)
- Rate performance significantly improved compared to 2-layer design
- Insignificant effect from laser structuring due to large pitch and relative thin electrode (126 µm)
- Future work will be increasing electrode thickness and reducing pitch size

Karlsruhe Institute of Technology
Oak Ridge National Laboratory
National Transportation Research Center

Collaborations

- Partners
  - National Labs: Argonne National Laboratory, Sand National Laboratory, Idaho National Laboratory
  - Battery Manufacturers: XALT Energy, Navitas Systems
  - Active Material Suppliers: TODA America, Superior Graphite, ConocoPhillips, PneumatiCoat
  - Inactive Material Suppliers: JSR Micro, Solvay Specialty Polymers, Ashland, IMERYS
  - Equipment/Coating Suppliers: PPG Industries, Frontier Industrial Technology, B&W MEGTEC, DataPhysics
  - Universities: KIT, Binghamton University

- Collaborative Activities
  - Characterization of surface energy and electrolyte wetting with Binghamton University (weekly discussion) and Data Physics (quarterly discussion)
  - Laser structuring of thick electrodes with KIT (monthly discussion)
  - Binder selection and optimization with Solvay, Ashland, and JSR (bi-annual discussion)
  - Sharing of results with strategic battery manufacturers (Navitas Systems and XALT)

Future Work

- Remainder of FY18
  - Demonstrate baseline fabrication procedure for Ni-rich NMC cathodes via aqueous processing and good electrochemical performance in pouch cells.
  - Characterize contact angle of electrolyte on electrodes.
  - Characterize electrolyte wetting into electrodes.
  - Analyze effect of laser structuring design on energy and power density.
- Into FY19
  - Fabricate thick electrodes with various active material particle sizes.
  - Optimize processing conditions for Ni-rich NMC cathodes via aqueous processing.
  - Develop and integrate unique electrode architectures to graphite anodes.
  - Demonstrate electrochemical performance in large format pouch cells.
  - Integrate next-generation active materials such as heterostructured and disordered cathodes.
- Commercialization: Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility; 2 patents issued.

Any proposed future work is subject to change based on funding levels

Summary

- **Objective:** This project facilitates lowering the unit energy cost by up to 17% by addressing the expensive electrode coating and drying steps while simultaneously increasing electrode thickness.
- **Approach:** Develop green manufacturing with tailored electrode architectures to enable implementation of aqueous processed thick electrodes for high power performance.
  - Understand mass transport limitation in high energy electrodes.
  - Develop electrode formulation and processing to enable thick electrode manufacturing.
  - Develop tailored electrode architecture to overcome mass transport limitation.
  - Integrate aqueous processing with high energy high voltage cathode materials.
  - Demonstrate and validate electrochemical performance in large format pouch cells.
  - Characterize surface energy of electrodes and evaluate electrolyte wetting in thick electrodes.
- **Technical:** Fabricate thick and crack-free NMC532 cathodes (4 mAh/cm^2) via co-solvent; Demonstrate 225 Wh/kg in pouch cells with NMC532 and graphite electrodes; Characterized compatibility of NMC811 with aqueous processing; Demonstrated excellent rate performance and cyclability of aqueous processed NMC811 cathodes; Created laser structured electrodes; Characterized surface energy of electrodes.
- **Collaborators:** Extensive collaborations with national laboratories, universities, lithium-ion battery manufacturers, raw materials suppliers, and coating producer.
- **Commercialization:** 2 patents issued; high likelihood of technology transfer due to significant cost reduction benefits and equipment compatibility.

Selected Responses to Specific FY17 DOE AMR Reviewer Comments

- Second reviewer commented that a broad group of partners is working on this project, the roles of several of the partners are specifically identified, and the future roles of industrial partners are mentioned. There are no explicit details about how the partners actually interact or how often.
  - **Details about the actual interaction and frequency for FY18 have been recorded in slide 16**
- Fifth reviewer commented that the project approaches the goals from multiple angles and addresses the cost and performance barriers. However, some of the directions may be straying from the goals. For example, it is not clear if the laser structuring of the electrode will not completely cancel the cost advantages and throughput of aqueous processing. An approach based on slurry formulation and coating conditions would be less inexpensive in mitigating the power and polarization issues.
  - **The reviewer was right. The laser structuring will introduce additional processing cost and reduce the throughput. However, this is to address mass transport limitation in thick electrodes which also exists in NMP-based processed electrodes. There is still cost reduction in laser structured and aqueous processing. In addition, we are another approach based on NMP based slurry formulation (bat266) in mitigating mass transport issue. Once the technique is developed, we will leverage the technology with aqueous processing.**
- Fourth reviewer pointed out that laser structuring for electrolyte transport inside electrodes will improve C-rate capabilities, but also will have a negative impact on energy density and cost of electrodes. The reviewer asked if it were possible to quantify these impacts.
  - **Yes, it's possible to quantify the loss in energy density. A similar work can be found in Journal of the Electrochemical Society, 164(7) (2017), A1339-A1341. The energy and power density at high rate is actually increased.**

Acknowledgements

- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Program Managers: David Howell and Peter Faguy)

- ORNL Contributors:
  - David Wood
  - Claus Daniel
  - Zhijia Du
  - Yangping Sheng
  - Seong Jin An
  - Marissa Wood
  - Kevin Hays
  - Jesse Andrews
  - Tommiejean Christensen

Technical Collaborators:
- Robert Wang
- Congrui Jin
- James Banas
- Gregg Lytle

Information Dissemination and Commercialization

- **7 Refereed Journal Papers and Patents**

1. Zhijia Du, Jianlin Li, Marissa Wood, Chengyu Mao, Claus Daniel, and David Wood, “Three-dimensional conductive network formed by carbon nanotubes in aqueous processed NMC532 electrode”, *Electrochimica Acta*, 270 (2018) 54-61.

2. Hsiu-Ling Tsai, Chien-Te Hsieh, Jianlin Li, and Yasser Ashraf Gandomi, “Enabling high rate charge and discharge capability, low internal resistance and excellent cyclability for Li-ion batteries utilizing graphene additives”, *Electrochimica Acta*, 273 (2018) 200-207.

3. David Wood, Jeffrey Quass, Jianlin Li, Shabbir Ahmed, David Ventola, and Claus Daniel, “Technical and economic analysis of solvent-based lithium-ion electrode drying with water and NMP”, *Drying Technologies*, 36(2) (2018) 234-244.

4. Hui Zhang, Chengyu Mao, Jianlin Li, and Ruiyong Chen, “Nanomaterials for lithium-ion batteries”, *RSC Advances*, 7 (2017), 33789-33811.

5. Seong Jin An, Jianlin Li, Claus Daniel, Sergiy Kalnaus, and David Wood, “Design and demonstration of three-electrode pouch cells for lithium-ion batteries”, *Journal of the Electrochemical Society*, 164 (7) (2017), A1755-1764.

6. Jianlin Li, Zhijia Du, Rose Ruther, Seong Jin An, Lamuel David, Kevin Hays, Marissa Wood, Nathan Phillip, Yangping Sheng, Chengyu Mao, Sergiy Kalnaus, Claus Daniel, and David Wood, “Towards low-cost, high energy density and high power density lithium-ion batteries”, *JOM*, 89(9) (2017), 1484-1496.

7. Jianlin Li, Beth Armstrong, Claus Daniel, and David Wood, “Aqueous processing of composite lithium ion electrode material”, US Patent No. 9,685,652 B2, June 20, 2017.

- **Selected Presentations**

    1. Jianlin Li, “Technical and economic analysis of solvent-based lithium-ion electrode drying with water and NMP”, 2018 International Battery Seminar, Fort Lauderdale, FL, March 26-29, 2018. **(Invited)**